EVIDENCE FOR FORMATION OF MOLECULAR GROUPS IN LIQUIDS AT LOW TEMPERATURES*

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(*Received for publication, July* 24, 1958)

ABSTRACT. The intensity-distribution in the wing accompanying the Rayleigh line scattered by pyridine, *a*-picoline, *o*-cresol, *o*-chlorophenol and *p*-xylene at temperatures near about the freezing points of the liquids has been studied by the method of photographic spectrophotometry and it has been compared with that observed at higher temperatures in each case. It has been found that in all the cases the intensity of the wing in the region from the centre of the Rayleigh line upto a distance of about 25 cm^{-1} decreases with the lowering of temperature and at the lower temperature there appear in the wing at distances beyond 45 cm^{-1} from the Rayleigh line additional intensities from new sources. The intensity of the wing beyond 45 cm^{-1} due to the liquid at low temperatures has been compared with the intensity of the low-frequency Raman lines observed in the region 45–137 cm^{-1} in the spectra due to the frozen liquids. It has been concluded that the additional intensity mentioned above may arise from vibration in groups of loosely attached molecules formed in the liquid near its freezing point and that the size of these groups and also the strength of the intermolecular bond in the groups increase with solidification of the liquid.

INTRODUCTION

The intensity-distribution in the wing accompaying the Rayleigh radiation scattered by various substances in gaseous and liquid states has been studied by many workers and different workers have put forward different hypotheses to explain the origin of the wing. Bhagavantam (1933) pointed out that most of the liquids cannot be treated as aggregates of freely rotating molecules and as such the theory developed in the case of gases does not apply to the liquids. From theoretical considerations he suggested that the intensity in the wing due to the liquids might arise from superposition of contributions from the partly gas-like and partly solid-like character of the liquid state. Gross and Vuks (1935), on the other hand, attributed the origin of the wing to vibrations of lattices in quasi-crystalline liquids analogous to those in the solid state. Later, Bhagavantam (1935) postulated that the hindered rotation of molecules pivoted in the lattice-like structure of the liquid was responsible for the occurrence of the wing. Rousset (1935), however, pointed out that for the amplitudes of hindered oscillations proposed

* Communicated by Prof. S. C. Sirkar.

by Bhagavantam (1935), the intensity of the wing for large frequency-shifts would be quite negligible and postulated the influence of formation of cybotactic groups in the liquid state on the rotational energy levels of the freely rotating molecules. He also considered the broadening of the exciting Rayleigh line due to the fluctuation of the intermolecular field caused by the impact of neighbouring molecules on the scattering centres as pointed out by Cabannes and Rocard (1929). Sirkar (1936) and Sirkar and Mookerjee (1936) made thorough investigations of the intensity-distributions in the wings due to some aliphatic and aromatic organic compounds in the liquid state and in sloutions and pointed out that the results obtained by them were not in complete agreement with the hypotheses put forward by the previous workers mentioned above. Sirkar and Mookerjee (1936) concluded that the intensity in a portion of the wing near the Rayleigh line might be produced by both rotational Raman scattering and broadening of Rayleigh line due to fluctuation of intermolecular field as pointed out by Cabannes and Rocard (1929), and the other portions of the wing might be due to vibrations of associated groups of molecules present in the liquid state. They also showed that the intensity in the wing depends on the anisotropy and nature of grouping of the molecules in the liquid state and that the major portion of the wing is in no way connected with the new Raman lines which are observed in the low-frequency region in the case of the solid state. Similar conclusions were also arrived at by Pniewski (1938a, b) from results of investigations on the wing due to carbon disulphide, chloroform and carbon tetrachloride. Gross and Raskin (1945) suggested that vibrations of molecules in the liquid analogous to those of the molecules in the lattice might give rise to the wing. Raskin (1948), however, concluded more recently from the results of investigations on the low-frequency Raman lines and the wing accompaying Rayleigh line due to phenol and diphenyl methane that the phenomenon of the wing cannot be treated as evidence of persistence of quasi-crystalline remnants in the liquid state.

The different hypotheses mentioned above do not seem to agree with each other completely and it appears that no single hypothesis is sufficient to explain the orign of the whole portion of the wing satisfactorily. So, it was intended to test the correctness of the various view points and to obtain some information which might lead to an unequivocal conclusion regarding the origin of the different portions of the wing. For this purpose the dependence of distribution of intensity in the wing due to a few typical aromatic liquids on temperature has been investigated quantitatively and the results have been discussed in the light of the various hypotheses mentioned above.

EXPERIMENTAL

In order to study the distribution of intensity in the wing due to any liquid at different temperatures ranging from −70°C to 150°C, three different arrangements were made. The experimental arrangement used in photographing the

spectra of the light scattered by the liquids at temperatures below 0°C was the same as that used for studying the wing due to liquid oxygen (Kastha, 1954). A mixture of liquid oxygen and ethyl alcohol at a definite proportion was used to obtain a bath at a particular low temperature which was measured with a pentane thermometer, For temperature above 0°C but below 20°C, the Dewar vessel and the liquid container were replaced by a double jacketed Wood's tube through which cold water maintained at proper temperatures was circulated with a pump. The temperature of the outgoing water was measured and kept constant within 1°C. For temperatures above 100°C the liquid in its container was placed in a cylindrical heater provided with two long slits parallel to the axis.

The liquids investigated were pyridine, α-picoline, *o*-cresol, *o*-chlorophenol and para-xylene. These were supplied by E. Merck, Fischer Scientific Co. and B. D. H. Each of the liquids was fractionated and the proper fraction was repeatedly distilled under reduced pressure to make it dust-free.

The spectrograph used in the present investigation has a dispersion of about 11 A.U./mm in the region 4047 A.U. and on the Stokes side the line is absolutely free from coma. This line was therefore chosen to study the distribution of intensity in the wing due to the liquid at different temperatureres.

The same slit width was used throughout the investigation. Ilford Zenith plates were used to photograph all the spectra and since a quantitative measurement of intensity was aimed at the exposures were so adjusted as to give a clear background and Raman lines of suitable densities in the spectrograms.

The microphotometric records of the various spectrograms were taken with a Kipp and Zonen self-recording microphotometer of the Moll type using a 8 : 1 magnification ratio.

The details of the method followed in converting the blackening due to the wing and the Raman lines into intensity readings and for obtaining the relative intensity-distribution in the wing taking into account the widening of the Rayleigh line, were the same as described in an earlier paper (Kastha, 1954). The intensities $I_{\Delta\nu}$ at distances $\Delta\nu$ from the centre of the Rayleigh line 4047 A.U. due to any of the liquids at a given temperature were compared with the intensity of a suitable Raman line (I_R). The lines 654 cm^{-1} in the case of pyridine and the line 810 cm^{-1} in the case of α-picoline were used as the reference Raman lines. The Raman lines 680, 750 and 647 cm^{-1} served as reference lines in the case of *o*-chlorophenol, *o*-cresol and *p*-xylene respectively. The values of $I_{\Delta\nu}/I_R$ were plotted against the distances $\Delta\nu$ from the centre of the Rayleigh line to obtain the true intensity-distribution in the wing for the liquid at the particular temperature. Such data obtained for the liquid at different temperatures furnished information regarding the dependence of the intensity of any portion of the wing on temperature.

RESULTS

The curves showing the distribution of intensity in the wing accompaying the Hg line 4047 A.U. scattered by the liquids at different temperatures are reproduced in figures 1-5. The changes in the intensity-distribution which take place with change of temperature of the different liquids studied in the present investigation are stated below.

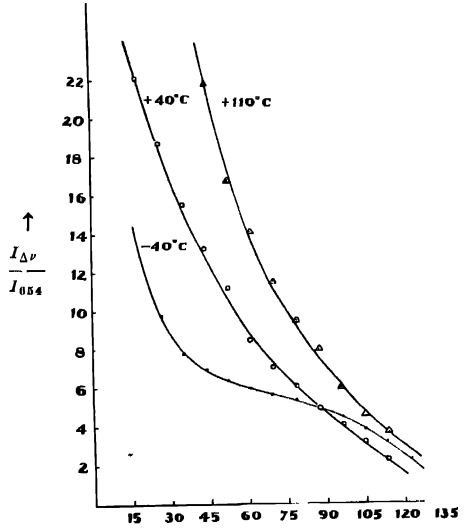

Fig. 1. Pyridine

(a) *Pyridine*: It can be seen from figure 1 that the intensity in the wing due to pyridine at 40°C is large at distances less than 25 cm^{-1} and beyond this distance it gradually decreases with increasing distances from the centre of the Rayleigh line. When the temperature of the liquid is raised to 110°C the intensity of the portion of the wing lying within 40 cm^{-1} from the Rayleigh line increases remarkably while that of the portion beyond 40 cm^{-1} increases only slightly. When the liquid is cooled to −40°C the intensity-distribution in the wing changes completely and the intensity at each point in the wing upto 90 cm^{-1} is reduced considerably. It is also found that at −40°C throughout the region between 45–90 cm^{-1} the intensity at different points is almost the same, but beyond 90 cm^{-1} the intensity at any point in the wing is larger than that observed in the case of the liquid at 40°C. The wing however extends upto 140 cm^{-1} at both the temperatures.

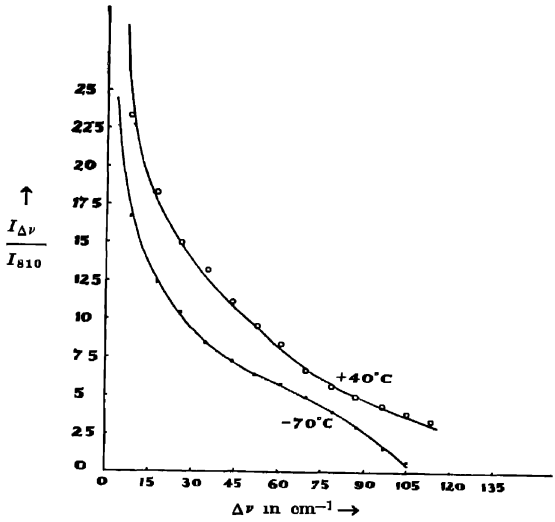

Fig. 2. α-Picoline

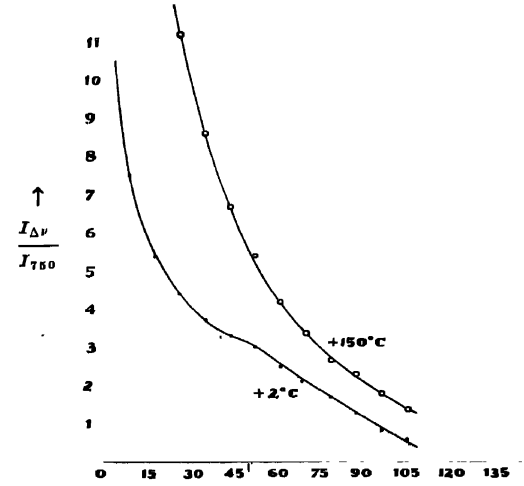

Fig. 3. o-Cresol

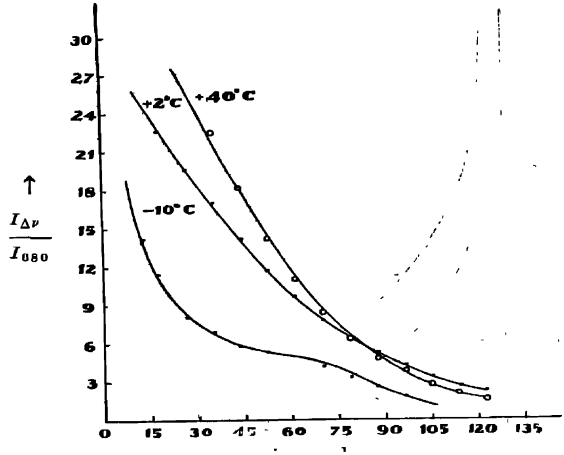

Fig. 4. *o*-Chlorophenol

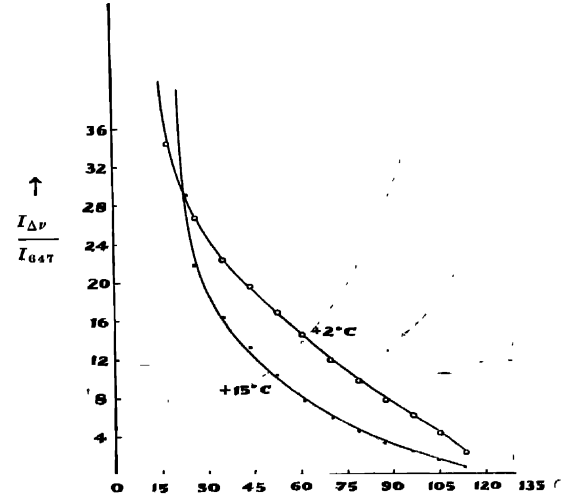

Fig. 5. *p*-Xylene

(b) *α-picoline* : It is seen from figure 2 that the intensity-distribution in the wing due to this liquid at 40°C is similar to that observed in the case of pyridine at the same temperature. When the liquid is cooled to −70°C the intensity in the region very near to the Rayleigh line is greatly reduced and an inflexion in the intensity-$\Delta\nu$ curve appears at about 45 cm^{-1}, beyond which the intensity slowly decreases to zero at about 105 cm^{-1}.

(c) *o-Cresol* : In this case when the liquid is super cooled to 2°C (figure 3) the intensity of the wing close to the Rayleigh line is greatly reduced and an inflexion in the intensity-distribution curve appears at 45 cm^{-1}. The intensity of the wing beyond 45 cm^{-1} falls off rapidly and becomes negligible at about 110 cm^{-1}.

(d) *o-Chlorophenol* : In this case the intensity-distribution in the wing due to the liquid at 40°C and 2°C shown in figure 4 is similar to that observed in the case of pyridine at 40°C. The intensity-distribution curve for *o*-chlorophenol at −10°C is similar to that in the wing due to pyridine at −40°C, but in the former case the intensity extends upto 120 cm^{-1}.

(e) *p-Xylene* : It can be seen from figure 5 that the intensity-distribution curves due to *p*-xylene at 2°C and 15°C respectively intersect each other at about 25 cm^{-1} and that the intensity beyond 25 cm^{-1} from the Rayleigh line increases while that in the portion nearer to the Rayleigh line diminishes considerably when the liquid is cooled to 2°C.

DISCUSSION

The results described above indicate that in all cases the intensity in the region adjacent to the Rayleigh line is very large and it increases rapidly with the rise of temperature of the liquids and diminishes considerably when the temperatures of the liquids are lowered. The intensity at large distances from the Rayleigh line, however, increases in the case of *p*-xylene and pyridine and diminishes in other cases when the liquids are cooled to low temperatures. The above-mentioned changes in the intensity of the portion of the wing near to the Rayleigh line, with change of temperature of the liquids, suggest that a part of the intensity in this portion of the wing may be due to rotational Raman scattering. Another part may arise out of contributions from Rayleigh radiation broadened in the process of scattering of light by molecules in motion due to collision as suggested by Cabannes and Rocard (1929). According to the theory of rotational Raman scattering the intensity of the wing would be zero at the centre of the Rayleigh line and a maximum of intensity in the wing would be expected at distances varying from 8 cm^{-1} to 18 cm^{-1} from the centre of the Rayleigh line due to the different liquids studied. On this would be superposed the intensity of the edges of the broadened Rayleigh radiation mentioned above. The relative contributions to the intensity of the wing

from these two causes cannot be determined from the results obtained, because the intensity-distribution in the wing at distances less than 15 cm^{-1} from the Rayleigh line could not be determined on account of insufficient dispersion of the spectrograph used and the blackening produced in the neighbourhood of Rayleigh line due to scattering in the photographic emulsions. Since the forces hindering rotations and other type of movements of the molecules increase with lowering of temperature of the liquid, the intensity of the portion of the wing close to the Rayleigh line is expected to decrease when the liquids are cooled to low temperatures. However, the increase in the intensity of the wing beyond 25 cm^{-1} and 90 cm^{-1} in the case of *p*-xylene at 2°C and pyridine at –40°C respectively indicates clearly, that the intensities in these regions of the wing are not wholly due to rotational scattering or to broadening of Rayleigh line arising out of molecular collisions. Moreover, since it is known that almost all the molecules of *o*-chlorophenol in the liquid state exist as dimers at room temperature (Pauling, 1945, Sirkar *et al.*, 1958) and the motion of these dimers is hindered to a greater extent when the temperature of the liquid is lowered, the intensity in the wing at distances beyond 50 cm^{-1} from the Rayleigh line which diminishes only slightly with lowering of temperature to –10°C, cannot be due either to rotation or to collisions of the molecules. Thus it seems plausible to assume that a major part of the intensity of the wing at distances beyond 50 cm^{-1} from the Rayleigh line observed in the present case originates from vibrations of groups of molecules which are formed in the liquids at low temperatures and since some of these groups of molecules would be expected to break up with increase of temperatures the contribution due to vibrations of such groups to the intensity of the part of the wing mentioned above, would diminish at higher temperatures. Also, as there is some contribution to the intensity in this part of the wing from rotational scattering these groups are small enough to permit rotation of other free single molecules. It must be pointed out, however, that these groups are different from the cybotactic groups postulated by Rousset (1935). Since the latter groups give rise to X-ray diffraction haloes, the size of the groups must be large and as such groups are continuously formed and broken within the volume of the liquid the binding forces between adjacent molecules in those groups are small and the intensity of the wing at large distances from the Rayleigh line cannot be attributed to any intermolecular vibration in such groups. Moreover, the appreciable intensities beyond 50 cm^{-1} observed in the wing due to these liquids at low temperatures indicate that the groups are formed by molecules attached to each other through weak linkages. These forces are stronger than the Van der Waals' forces but much weaker than the forces due to regular bonding. The continuous nature of the scattering due to vibrations in such groups in the liquid may be due to the fact that the frequencies of vibrations of these groups of molecules overlap each other on account of fluctuations in the strength of binding due to impact of neighbouring molecules. Formation of such groups of

molecules in the liquid state was also inferred by Sirkar and Mookerjee (1936) from results of investigation of the wing due to a few organic liquids in the pure state and in solutions and by Pniewski (1938a, b) who measured the intensity in the wings due to CS_2, $CHCl_3$ and CCl_4.

In this connection it would be interesting to compare the intensity-distribution in the wing due to the liquids at low temperatures with the intensities and positions of the low-frequency Raman lines which are observed in the spectra when the liquids are solidified. For this purpose, the positions of the low-frequency lines and their intensities estimated visually with respect to the intensity of a Raman line chosen in each case for obtaining the intensity-distribution in the wing due to the liquid are given in Table I. The figures in parentheses indicate these intensities.

TABLE I

Substance	Reference Raman line (R) $\Delta\nu$ in cm^{-1}	Low-frequency Raman lines $\Delta\nu$ in cm^{-1}			
Pyridine (-180°C) (Kastha, 1956)	654	58 (1)	82 (1)	97 (1)	137 ($\frac{1}{2}$)
α-Picoline (-180°C) (Kastha, 1957)	810	45 ($\frac{1}{2}$)	70 ($\frac{1}{2}$)	94 (1)	
o-Chlorophenol (-30°C) (Biswas, 1954a)	680	51 ($\frac{1}{2}$)	63 ($\frac{1}{2}$)	94 (1b)	
o-Cresol (-30°C) (Biswas, 1955)	750	45 ($\frac{1}{2}$)	90 (1b)		
p-Xylene (-30°C) (Biswas, 1954b)	647	55 ($\frac{1}{2}$)	91 (4b)		

It can be seen from Table I and figures 1–5 that the low-frequency lines appear in each case in regions which correspond to those in the wing due to the liquid state at low temperature in which there is continuous Raman scattering which has been attributed to vibrations in groups of molecules. Also, the low-frequency lines are not observed in other regions in which the wing has no appreciable intensity. These facts suggest that the same groups of molecules which are responsible for the intensity observed in the wing beyond 45 cm^{-1} due to liquids at low temperatures are also responsible for the origin of the low-frequency lines which appear in the spectra when the liquids are frozen. It can be seen from figures 1–5 and Table I that the intensity of the low-frequency lines taken together is much less than the aggregate intensity of the wing beyond 45 cm^{-1} in all cases. Since the variation in the strength of binding among the molecules in the groups due to impact from neighbouring molecules ceases as the liquids are frozen, the frequencies of vibrations due to these groups are expected to become discrete in the solid state. The dimunition in the intensity of these lines may be explained

in the following way. When the liquid is frozen the groups of molecules mentioned above may link up with other neighbouring groups to form larger aggregates in the solid state. In some modes of vibrations of the groups in the liquid state involving angular motions, the change in the polarisibility produced in some of the smaller groups of molecules diminishes enormously in the solid state because of restriction of such modes in the larger groups. Also the scattering arising from rotation of some individual molecules still present in the liquid state ceases completely with solidification of the liquids. These two reasons taken together may account for the feebleness of the low-frequency lines compared to the intensity of the part of the wing beyond 45 cm^{-1} due to the liquids at low temperatures.

These results thus indicate the formation of groups of molecules in the liquid state and increase in the size of these groups with solidification of the liquids. The large frequency-shifts of the low-frequency Raman lines also indicate that the binding forces between the molecules in these groups are much larger than Van der Waals' existing in the liquids at ordinary temperatures. If the melting point of the crystal be slightly below the room temperature, groups of molecules may be present in the liquid even at the room temperature, as in the case of diphenyl ether (Sirkar, 1936).

ACKNOWLEDGMENTS

The author's grateful thanks are due to Professor S. C. Sirkar, D.Sc., F.N.I., for his kind interest during the progress of the work.

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